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COMPLEXES CONTAINING COBALT, MOLYBDENUM AND TUNGSTEN

HARRY A. ALSENTZER, JR.

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
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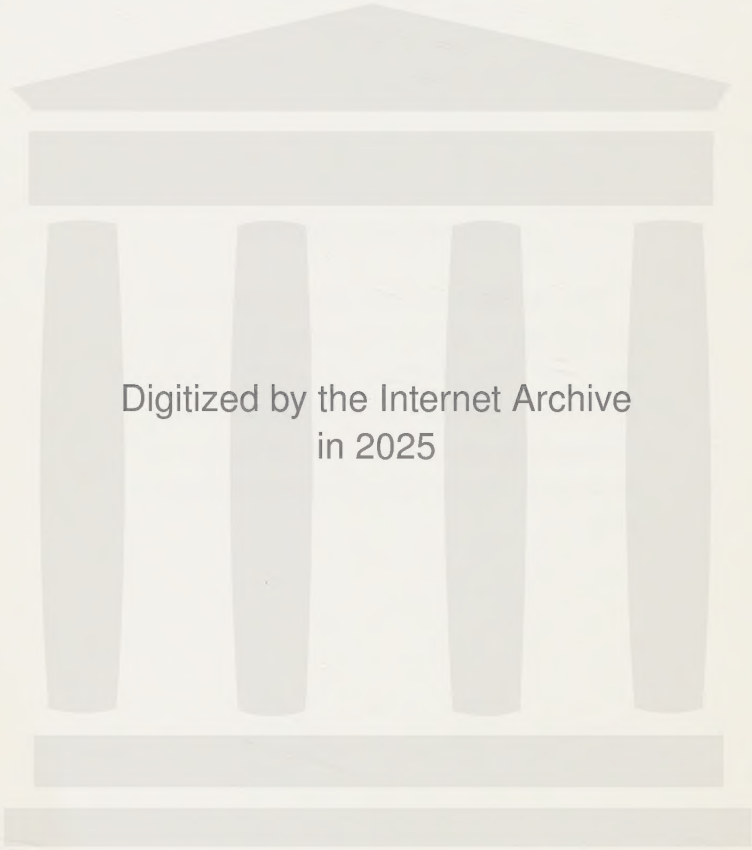
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I

INTRODUCTION

In this investigation normal tungstates and molybdates of the chlorpentammine and brompentammine cobaltic complexes were prepared. A method was discovered for the preparation of a complex salt containing cobalt and molybdenum in the anion, from a cobaltammine containing trivalent cobalt in the cation. A new compound containing cobaltous cobalt and tungsten in the complex anion was prepared. New methods for the decomposition and analysis of the salts were tried. A separation of halogen from molybdenum and tungsten was devised, using barium hydroxide.

Only a few cobaltic compounds containing molybdenum or tungsten are described in the literature. Phosphomolybdates of the chlorpentammine cobalt series were prepared by Jörgensen.[1] A. Carnot[2] added acetic acid and ammonium molybdate to a solution of chlorpentammine-cobalti-chloride and obtained an insoluble compound with a peach blossom color. He dried the compound at 100° and wrote the formula $Co_2O_3 \cdot 5NH_3 \cdot 7 MoO_3 \cdot 3H_2O$. He failed to mention the displacement of the chlorine from the stable complex cation. In a later paper, Carnot recommended this salt for the quantitative determination of cobalt by drying at 110° which he claimed eliminated water but no ammonia. Friedheim and Keller[3] investigated the green compounds $3(NH_4)_2O \cdot CoO \cdot CoO_2 \cdot 12\ MoO_3 \cdot 20\ H_2O$ and $2(NH_4)_2 O \cdot CoO \cdot CoO_2 \cdot 10MoO_3 \cdot 12H_2O$ which are discussed later in this paper.

Gonzales[4] and Rosenheim[5] described rose-colored crystalline precipitates which were found to vary in composition depending on the concentration of the cobalt solution from which they were precipitated. Rosenheim formulated one of the compounds,

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[1] J. prakt. Chem. 18, 240 (1878).
[2] Comptes Rendues 108 (1889).
[3] Ber. 39, 4301 (1906).
[4] J. prakt Chem. (2) 36, 49 (1887).
[5] Z. anorg. Chem. 96, 139 (1916).

analyzing $2Na_2O \cdot 3CoO \cdot 12WO_3 \cdot 41H_2O$ as $Na_4Co_3H_{10}[H_2(WO_4)_6]_2 \cdot 34\ H_2O$. Carnot also described ammonium cobaltous tungstates of various composition which were rose colored.

II

ANALYTICAL PROCEDURE

Decomposition of Complex

The usual procedure for the decomposition of a cobaltic complex, is boiling with a strong solution of alkaline hydroxide thereby precipitating cobaltic hydroxide. Complexes containing volatile acid radicles or ammonia, are often decomposed by heat alone or evaporation and heating with concentrated sulphuric acid.

In view of the unusual nature of the acid radicles, and with a desire to avoid the use of strongly alkaline solutions with their attendant silica and other acid content, an attempt was made to decompose these complexes by other methods.

With the molybdenum compounds, a series of decompositions by heating in a stream of dry hydrogen chloride gas was undertaken, with the purpose of volatilizing the molybdenum content as $MoO_3 \cdot 2\ HCl$. The complex was placed in a porcelain boat in a long hard glass tube terminating in two water traps, and slowly heated while a stream of dry hydrogen chloride was passed over it. Decomposition began around 200° C, as evidenced by a color change in the salt and evolution of the voluminous oxychloride. Approximately thirty decompositions were carried out with the chlorpentammine molybdate and the ammonium cobalti-hexamolybdate. According to Browning[1] the temperature for volatilization lies between 250°–270° C. The writer believes that this temperature range is rather high and that the optimum temperature is around 240°. At the higher temperatures, 225°–250° C, it was found that cobalt chloride either

[1]Introduction to *The Rarer Elements*, John Wiley & Sons, 1917.

volatilized or was carried over mechanically by the oxychloride, giving low cobalt results. Baxter and Dorcas[2] purified cobaltous chloride for atomic weight work by sublimation above 300° C. They also state that cobalt chloride fuses before it sublimes. In certain runs, at the higher temperature, evidence of fusion was present, black spots appearing, which were found to contain molybdenum.

The wooly mass of oxychloride was frequently not white in color, varying from yellow to green to brown. This was ascribed to lower oxychlorides. To prevent this, dry oxygen gas was mixed with the hydrogen chloride, or oxygen and hydrogen chloride were passed alternately through the tube for short periods. On heating at lower temperatures 210°–225°, to prevent volatilization of cobalt chloride, it was found to be impossible to remove all of the molybdenum content from the boat. From a few of the results given below, it is evident that at higher temperatures, cobalt is lost and at lower temperatures molybdenum remains unvolatilized and that the method is not satisfactory for complete analysis.

	CHLORPENTAMMINE		AMMONIUM COBALTI MOLYBDATE	
	% Co	% MoO_3	% Co	% MoO_3
225°–250°	15.59	42.38	3.89	
	16.99	42.52	4.46	
	17.13	42.64	4.52	
210°–225°	17.22	41.76	4.73	69.96
	17.26	42.01	5.07	69.76
			*7.01	69.85
Calculated	17.36	42.41	4.89	71.69

*Cobalt found to contain molybdenum.

[2] J. Am. Chem. Soc. 46, 362 (1924).

With several of the tungsten complexes, decompositions were attempted with concentrated acids. Evaporation to dryness with concentrated hydrochloric acid alone, or followed by concentrated nitric acid, failed on washing with water to yield tungstic oxide free from cobalt. It is therefore evident that the complexes are more or less stable in the presence of hydrogen ions and decomposition by alkaline hydroxides is necessary.

Determinatian of Constituents

Cobalt as Metallic Cobalt

Cobalt was first determined electrolytically from a sulphate solution containing sulphuric acid, using a mercury cathode. A current of 5 amperes at 6 volts for 30 minutes was used.

In making practice determinations a cobalt solution was taken and 5 ml. of concentrated nitric acid were added. Approximately a score of determinations was made, which varied considerably, before it was discovered that the nitric acid was partially reduced to ammonia, forming ammonium amalgam, as was proven by shaking the mercury cathode with dilute hydrochloric acid and testing the latter with Nessler's reagent.

The method using sulphuric acid, although reliable, was discarded since it was necessary to evaporate the cobalt chloride solution to dryness with sulphuric acid before electrolysis, to expel the chlorine.

As $CoNH_4PO_4$ or $Co_2P_2O_7$

The precipitation of a neutral cobalt solution by a neutral solution of sodium phosphate as recommended by Schoeller and Powell[3] and others, was given a thorough trial.

The precipitation of cobalt is not complete and doubt as to the composition of the crystalline carmine red precipitate is evidenced by the following comparison of the cobalt content,

[3] *Analyst* XLII, page 189, (1917); XLIV, page 275 (1919).

weighing first as $CoNH_4PO_4$, and after ignition weighing as $Co_2P_2O_7$. A few of the results illustrate these conclusions.

$CoNH_4PO_4$	$Co_2P_2O_7$
Calculated as % Co	
Brompentammine Tungstate	
13.75	12.36
13.54	12.06
	Calculated 12.49
Ammonium Cobalto Tungstate	
4.49	4.00
4.42	3.97
4.64	4.27
4.42	3.98
4.24	3.87

Congdon[4] found that in this method the cobalt in the filtrate from the phosphate must be precipitated as sulphide, ignited to oxide, and its weight added to that determined as above.

Nitroso–β–Naphthol Method

Congdon recommended the nitroso–β–naphthol precipitation method of Eder.[5] The nitroso–β-naphthol in 50% acetic acid is added to the cobalt solution made slightly acid with hydrochloric acid. The voluminous red precipitate is ignited with a small quantity of oxalic acid to prevent explosion and is weighed as Co_3O_4. This method gives satisfactory results and is easily carried out.

As $CoSO_4$

A few determinations were made as $CoSO_4$. The cobalt solution was evaporated with sulphuric acid and then heated until the excess of acid is decomposed. This method was abandoned since sodium salts were usually present in the cobalt solution.

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[4] *Chem. News*, 1924.
[5] *Chem. Zeit* XLVI, 430 (1922).

Molybdenum

Molybdenum was determined gravimetrically as $PbMoO_4$. At first the method of Schoeller and Powell[6] was employed. This consists of precipitating the boiling molybdate solution containing ammonium chloride, ammonium acetate, and acetic acid, with a dilute solution of lead acetate, until no further precipitate appears. The lead molybdate is then washed with dilute ammonium acetate until the filtrate fails to give a coloration with sodium sulphide. This washing is a tedious operation, and unless strictly adhered to gives high results as shown by the following determinations:

Ammonium Cobalti Molybdate
% MoO_3
72.54
73.20
72.61
73.58
72.37
Calculated 71.69

The method of Bonardi[7] is essentially identical with the one important exception, that the end point when all molybdenum has been precipitated, is determined with tannic acid as an outside indicator, thus preventing an excess of lead salts. This method, therefore, is to be preferred to that of Schoeller and Powell; is easily carried out and gives excellent results.

Tungsten as Mercurous Tungstate

Tungsten was first determined by precipitation as mercurous tungstate, according to Schoeller and Powell (text). The alkaline tungstate solution is made just acid to methyl orange with nitric acid and then rendered alkaline with 2 drops of a

[6] *The Analysis of Minerals and Ores of the Rarer Elements*, Griffin and Co.' 1919.

[7] Analytical Methods for Certain Metals, Bulletin 212, U. S. Bureau of Mines.

25% solution of ammonium carbonate. It is then precipitated by the slow addition of a nearly neutral mercurous nitrate solution.

This method gives low results, as shown by a few of the determinations, due to the difficulty in maintaining a neutral solution; mercurous tungstate dissolving in nitric acid.

Chlorpentammine Tungstate

% WO_3	
53.54	53.36
53.50	53.87
53.76	

Calculated 54.26

Neutralization of the nitric acid in the mercurous tungstate precipitation, was then effected by adding an excess of a suspension of mercuric oxide in water. With this modification, the results became more constant and approached the calculated value.

% WO_3	
54.01	54.18
54.15	54.11
54.08	

Calculated 54.26

The method of Davis[8] gives excellent results. The soluble tungstate is treated with concentrated hydrochloric acid, followed by nitric acid, with evaporation to small volume, whereby most of the tungstic acid is rendered insoluble. The solution is then diluted and the small amount of tungstic acid remaining in solution, is precipitated by cinchonine as cinchonine tungstate. The precipitate, after filtering, is dissolved in warm ammonium hydroxide, the solution is boiled to expel excess of ammonia, and after acidulation, the tungsten is again precipitated by cinchonine. Ignition gives a pure yellow oxide.

[8] Bulletin 212, U. S. Bureau of Mines.

Halogen

The determination of chlorine or bromine in the presence of tungsten or molybdenum, presented an analytical problem for which no method was found in the literature.

Evolution Methods

The first method attempted was by the oxidation of the halogen to the free element and its determination by iodimetry. The complex was decomposed with alkaline hydroxide, the mixture of sodium halide and tungstate was then heated with potassium permanganate and sulphuric acid and the evolved chlorine led into a solution of potassium iodide, which was then titrated with sodium thiosulphate. The results were low and the method was discarded.

Evolution of the halogen as hydrogen chloride by heating with sulphuric acid, was then tried. The mixture of sodium halide and tungstate was evaporated to a small volume and then introduced into the apparatus used by E. C. Wagner[9] in his evaluation of potassium chlorate. Concentrated sulphuric acid was then added and the mixture heated until fumes of sulphur trioxide were evolved. The hydrogen chloride was driven by a slow stream of dry air into the absorption vessel which contained water and in some of the experiments dilute ammonium hydroxide. The chlorine content of the absorbing solution was then determined as silver chloride. This method also yielded low results.

Separation of Halogen From Molybdate or Tungstate by Barium Hydroxide

The method which proved satisfactory and was used for determination, consisted in decomposing the complex, by boiling with a solution of barium hydroxide, thereby precipitating the tungsten or molybdenum as the barium salt and the cobalt as cobaltic

[9] *Ind. Eng. Chem.*, 16, 616 (1924).

hydroxide. The barium halide solution was filtered, acidified with nitric acid and the halogen determined as silver salt.

Ammonia

Brönsted and La Mer[10] determined ammonia in cobaltammines by evolution with alkali, with absorption in 0.02 N hydrochloric acid and subsequent titration of the latter with methyl red. In a previous paper Brönsted and Petersen[11] recommend evolution with alkali, with or without the addition of reducing substances such as stannous chloride and the absorption in sulphuric acid.

The determinations were carried out in a pyrex Kjeldahl flask with a pyrex trap and a quartz water-cooled condenser. The distillations were carried out very slowly, during a 4 to 5 hour period, until approximately 75 cc of distillate had been absorbed.

With hydrochloric acid, the determinations were unsatisfactory. Brönsted and La Mer do not state that carbonate free hydroxide was used for the titration of the acid and since methyl red is somewhat sensitive to carbon dioxide, titration could only be carried out after boiling, and this did not recommend itself for hydrochloric acid solution.

With sulphuric acid and boiling before titration, the results became more concordant but still somewhat low. It was thought possible that the cobaltic cobalt of the complex might oxidize some of the ammonia. Reducing agents such as metallic tin and Devardo's alloy, were found to increase the percentage of ammonia and bring it almost to the calculated amount. One piece of Devardo's alloy about the size of a marble was used in each distilling flask throughout all of the determinations.

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[10] *J. Am. Chem. Soc.*, 46, 555, (1924).
[11] *J. Am. Chem. Soc.*, 43, 2265, (1921).

III

COMPOUNDS

Normal Molybdates and Tungstates of Cobaltammines

The usual method for preparing salts of a cobaltiammino cation is by metathetical reactions. Normal sodium tungstate and molybdate were added, at room temperature, to solutions of salts of a number of hexammino, pentammino, and tetrammino cobalti cations in equimolecular and varied proportions. In some instances a precipitate was at once formed, in others only on standing for some time and in a few, no precipitation could be obtained. In all precipitations only noncrystalline substances were obtained, usually pink in color. The same results were obtained with paramolybdates, with para and metatungstates.

The cobaltammines are more or less stable in presence of the hydrogen ion and are decomposed by the hydroxyl ion, and since the soluble sodium and ammonium molybdates and tungstates are hydrolytically decomposed, it was decided not to investigate noncrystalline compounds. Proof that some of the latter were of varying composition, was shown by analyzing portions which had remained in contact with the precipitating solution for different periods. The ratio of cobalt to tungsten or molybdenum was found to vary.

The same experiments were repeated at higher temperatures. Attempts to mix warm or hot solutions of the cobaltammine salt with the soluble tungstate or molybdate, and by cooling and stirring, to obtain a crystalline precipitate, also failed The amorphous precipitates were often brownish in color, indicating decomposition to cobaltic hydroxide.

When ice-cold solutions were mixed and kept below 10° for some time, it was found that the chlor and brompentammine cations formed both crystalline and noncrystalline precipitates with the normal tungstate and molybdate. The other cations studied failed to yield crystalline substances, with either the normal or polymolybdates or tungstates.

$$\left[\begin{array}{c} (NH_3)_5 \\ Co \\ Cl \end{array}\right] WO_4$$

CHLORPENTAMMINE COBALTI TUNGSTATE

Preparation:—

To a solution of chlorpentammine cobalti chloride (prepared according to Sörensen[1]) saturated at 8°–10° C, was added a cold solution of normal sodium tungstate, in equimolecular proportions. On mixing, only slight precipitation was apparent, the liquid becoming opalescent. After standing for about 12 hours in the ice box (8°–10°) crystals were found to be growing on the sides of the beaker while a pink amorphous precipitate had settled to the bottom. The crystals continued to form for about 24 hours longer, when further growth stopped. If the liquid is not kept below 10° C, hydrolysis takes place and decomposition ensues.

The crystals can be separated from the amorphous precipitate by difference in specific gravity, repeated decantation with ice water removing the noncrystalline precipitate. The crystals are then washed with alcohol and ether and air dried. The amorphous precipitate was found to vary in composition.

Physical properties:—

Purple-red crystals, practically insoluble in ice water, slightly soluble in water at 20° C. Crystal system—Orthorhombic. Habit—tabular or prismatic. When the crystals are first formed, they appear as diamond-shaped tablets; on further growth, the enlargement is in the direction of the c axis, prisms being formed. Most crystals show simply the unit prism (110) and basal pinacoid (001). Prism angles measured on (001) average 113° and 67°, measurements being made by means of the petrographic microscope.

Optical properties:—

Biaxial +. Indices:— α 1.725±0.005; β 1.740±0.005; γ 1.760 ± 0.005, (determined by the immersion method in day-

[1] Z. anorg. Chem. 5, 369 (1894).

light). Optic plane ⊥ to c axis. X = b, Y = c, Z = a. Dispersion slight $\rho > v$. Pleochroism:—strong; X orange; Y red; Z violet.

Analysis:

Percentage Found	Co	WO_3	Cl	NH_3
	13.57	54.01	8.22	19.83
	13.71	54.15	8.12	19.86
	13.49	54.08	8.12	19.86
	13.52	54.18	8.20	
	13.65	54.11	8.17	
Calculated.....	13.79	54.26	8.29	19.92

Cobalt determined electrolytically.
Tungsten by precipitation with $HgNO_3 + HgO$.

$$\left[\begin{matrix} & (NH_3)_5 \\ Co & \\ & Br \end{matrix}\right] WO_4$$

BROMPENTAMMINE COBALTI TUNGSTATE

Preparation:—

Similar to that of chlor compound from brompentammine-cobalti-bromide (prepared from aquopentammine-cobalti-oxalate). Less amorphous precipitate is formed, which might be predicted, since the brom cation is not as acidic in nature as the chlor cation.

Physical properties:—

Purple-red crystals, slightly darker than the chlorpentammine tungstate. Insoluble in ice water. Crystalline form, habit and optical properties similar to chlor compound. Prism angles average 115° and 65°. As expected, the indices of refraction are slightly higher than in the chlor compound. α 1.745 ± 0.005;

β 1.760 ± 0.005; γ 1.825 ± 0.005. Pleochroism:—strong; X orange; Y violet-red; Z deep violet.

Analysis

Percentage Found	Co	WO_3	Br	NH_3
	12.75	49.13	16.45	17.85
	12.53	49.16	16.43	17.91
	12.74	49.04	16.48	17.98
	12.59	49.10	16.52	17.96
		49.27	16.46	17.93
			16.46	
Calculated.....	12.49	49.15	16.93	18.04

Co determined by nitroso-β-naphthol method.
WO_3 by quinine from acid solution.
Br low results attributed to hydrolysis in the preparation of the salt.

$$\left[\begin{matrix} & (NH_3)_5 \\ Co & \\ & Cl \end{matrix}\right] MoO_4$$

Chlorpentammine Cobalti Molybdate

Preparation:—

Similar to that of tungstate. Less amorphous precipitate since sodium molybdate is less alkaline than sodium tungstate.

Physical properties—

Dark red crystals, slightly soluble in ice water. Crystal system, habit, prism angles and optical properties similar to chlorpentammine tungstate. Indices of refraction slightly higher α 1.745 ± 0.005; β 1.753 ± 0.005; γ 1.780 ± 0.005.

Analysis:

Percentage Found	Co	MoO_3	Cl	NH_3
	17.13	42.48	9.25	24.99
	17.16	42.38	9.33	25.10
	17.19	42.48	9.27	25.05
	17.22	42.52	9.17	24.97
	17.26	42.64	9.21	
		42.44	9.24	
			9.25	
Calculated.....	17.36	42.41	10.44	25.08

Co determined electrolytically.
Cl—low results attributed to hydrolysis.

$$\left[\begin{array}{c} (NH_3)_5 \\ Co \\ Br \end{array}\right] MoO_4$$

BROMPENTAMMINE COBALTI MOLYBDATE

Preparation:—

Similar to that of brom-tungstate. Practically no amorphous precipitate obtained.

Physical properties:—

Purple-red crystals, insoluble in cold water. Crystal system, habit, prism angles and optical properties similar to that of brompentammine tungstate. Indices of refraction higher than chlor-molybdate and higher than brom-tungstate. α 1.769 ± 0.005 ; β 1.783 ± 0.005; γ 1.855 (estimated) ± 0.01.

Analysis:

Percentage Found	Co	MoO_3	Br	NH_3
	15.33	37.68	19.84	21.84
	15.40	37.60	19.65	22.12
	15.48	37.76	19.73	21.98
				22.01
Calculated.....	15.35	37.50	20.81	22.18

Co determined by nitroso–β–naphthol method.

Discussion of Pentammino Salts

In the preparation of the above salts, more amorphous precipitate was produced in the tungstate solutions than with sodium molybdate. This was ascribed to the alkalinity of the sodium tungstate in solution, or conversely, to the acidic nature of the cations converting a portion of the sodium tungstate to polytungstates, which were found in other experiments to yield only noncrystalline precipitates. Several partial analyses, already mentioned, of the amorphous precipitate, showed that the ratio of WO_3 to Co was greater than 1 to 1, although no definite ratio was obtained. This assumption, that the acidic nature of the cation partially decomposes the sodium tungstate or molybdate, is substantiated by the fact that the brompentammine ion, which is less acidic in character than the chlor, brings about the formation of less amorphous precipitate.

The crystals of the four salts are found to be in the orthorhombic system. Their crystalline habit is identical and their optical properties are very similar. As usual the increase in atomic weight from chlorine to bromine brings about an increase in index of refraction. Apparently, however, the increase in atomic weight from molybdenum to tungsten in the anion strangely brings about a slight lowering of the indices. As may

be seen from the values of the indices observed, the change from a chlor to a brom compound increases the birefringence in each case, while the transition from molybdate to tungstate has no effect. Whether or not this is a property of the atoms in question, or of their positions in the compound, can not be determined from the data available.

The Formation of a Complex Anion Containing Trivalent Cobalt From a Cobaltammine Cation

Many attempts were made to obtain cobaltammine cations with molybdenum in the complex with the cobalt atom, without success. As mentioned in the introduction a number of salts containing cobalt and molybdenum are described in the literature.

One of the salts already described was prepared by a method which was deemed of considerable interest. To a boiling solution containing about 100 ml. of a saturated solution of ammonium paramolybdate in a liter of water, was added a solution containing 1 gram of carbonato tetramminecobalti sulphate. A precipitate formed, which gradually changed in color from pink through lilac to gray-blue, and which finally dissolved to a green solution. This solution was concentrated to a volume of 400 ml. from which crystallized an emerald green compound. The filtrate on standing, yielded another crystalline compound, grass green in color. The emerald green crystals were recrystallized from hot water containing a few drops of acetic acid, dried with alcohol and ether and examined.

On analysis, the ratio of Co to MoO_3 was found to be 1 : 6. Both the color and this ratio identify the salt as one described by Freidheim and Keller[1] and by Muthmann and Nagel.[2] They prepared it by the oxidation of a solution containing cobalt acetate and ammonium paramolybdate with ammonium persulphate or by hydrogen peroxide and also obtained a dark green crystalline

[1] Ber., 39, 4301, (1906).
[2] Z. anorg. Chem., 24, 65, (1900).

compound (formulated in the introduction) from the mother liquor. Since Freidheim and Keller give no crystallagraphic data, the compound was examined and the following properties observed:

Crystal system—Orthorhombic—Habit—Tabular. Very flat, almost square tabular crystals, consisting essentially of basal pinacoid (001) and prism (110). Penetration twins common. Prism angles measured roughly on basal pinacoid average 94.5° and 85.5°.

Optical properties:—

Biaxal—Indices α 1.722 ± 0.005; β 1.750 ± 0.005; γ 1.772 ± 0.005. Optic plane $\perp$ to c axis. X=b, Y=c, Z=a. Dispersion moderate, $\rho > v$. Pleochroism—weak, X very pale green, Y green, Z blue-green.

Moderately soluble in water. The compound readily liberates chlorine from hydrochloric acid, proving the presence of trivalent cobalt. Freidheim and Keller formulate the salt $3(NH_4)_2O \cdot CoO \cdot CoO_2 \cdot 12\ MoO_3 \cdot 20\ H_2O$.

Since the coordination number of cobalt is usually six, this salt might be formulated according to the coordination theory of Werner

$$\left[Co(MoO_4)_6 \right] \begin{matrix} (NH_4)_3 \\ H_6 \end{matrix} \cdot 7H_2O$$

In the conversion from the carbonate tetrammine cation to the hexamolybdato anion

$$\left[Co \begin{matrix} (NH_3)_4 \\ CO_3 \end{matrix} \right]^{+1} \rightarrow \left[Co(MoO_4)_6 \right]^{-9}$$

we have the replacement of four ammonia molecules and a carbonate radicle occupying two coordination places by six acid

radicles which usually have a principle valence of two. This, however, is not uncommon since the carbonate, sulphite and sulphate radicles also form compounds in which they occupy only one coordination position.

Analysis:

Percentage Found		Co	MoO_3
		4.84	71.59
	a	4.73	71.90
		4.66	71.74
		4.73	
	b	5.07	
		5.06	
	c	4.96	71.88
		5.03	
Calculated		4.89	71.69

Cobalt determined (a) electrolytically, (b) $CoSO_4$, (c) nitroso-β-naphthol.

A Complex Containing Cobalt and Tungsten in the Anion

Attempts to prepare a cobalti-tungstate similar to the cobalti-molybdate failed. As mentioned in the introduction, only pink or rose-colored cobalt tungsten compounds have been reported in the literature. A green compound has been prepared which contains cobalt and tungsten in the anion. Crystallographic examination proves that the salt is homogeneous. Although its analysis has not been completed and its constitution therefore not yet determined, it was decided to report its preparation and reactions in this paper.

Preparation:—

To a boiling solution containing 50 grams of normal sodium tungstate and 25 ml. of glacial acetic acid in a liter of water, a solution containing 5 grams of cobaltous acetate is slowly added. The solution becomes red in color and on continued boiling a precipitate is formed, at first lilac in color, then changing gradually through gray to blue to blue-green, which finally dissolves to a blue-green solution. The latter is concentrated to a volume of 300 ml., filtered to remove a small quantity of a pink crystalline substance (which has not yet been investigated) and a solution containing 15 grams of ammonium chloride added. On cooling the green salt separates, mixed with crystals of ammonium tungstate. By several recrystallizations from hot water containing a few drops of acetic acid, the green salt can be purified.

Physical properties:—

Dark green crystals. Large crystals almost black. Crystal system—Isometric. Habit—Cubic. Index of Refraction—1.722 ± 0.005. Sparingly soluble in cold water; more soluble in hot water.

Chemical properties:—

The anion of the salt has been found to form insoluble compounds with ions of barium, calcium, silver, lead, mercurous mercury, and cobalt, and a sparingly soluble potassium salt. The compound does not oxidize hydrochloric acid even on warming, proving that only cobaltous cobalt is present.

Composition:—

The compound contains cobalt, tungsten, ammonia and water of crystallization.

A solution of the salt is stable toward acetic or dilute mineral acids, even on boiling. When an excess of mercurous or barium ion is added to a solution of the salt, an insoluble compound is formed (mercurous—green, barium—light blue); the filtrate is pink in color indicating cobaltous ion and contains a small quantity of tungstic acid in solution. The insoluble mercurous and barium salts, on decomposition, are found to contain approxi-

mately the same amount of cobalt as is present in the filtrate. Nitroso-β-naphthol produces an immediate precipitation of cobalt when added to a solution of the soluble green salt. This evidence indicates a structure

$$\left[Co_x(WO_4)_y \right] \begin{matrix} Co_x \\ (NH_4)_z \end{matrix}$$

The tungstic acid in the filtrate from the precipitated salts may be attributed to slight solubility of these so-called "insoluble compounds," or the presence of tungsten and even of some of the cobalt, might be due to a dissociation of the complex anion resulting in the following equilibrium:

$$\left[Co(WO_4)_n \right]^{-?} \rightleftarrows Co^{++} + WO_4^{--}$$

This explanation would be analogous to the complex ion theory proposed to explain the behavior of cobalt chloride in concentrated and dilute solutions

$$\underset{\text{(blue)}}{\left[CoCl_4 \right]^{--}} \rightleftarrows \underset{\text{(red)}}{CoCl_2} + 2\,Cl^{-}$$

The determination of the composition and constitution of the green salt and the series of insoluble compounds formed from it will be carried out and published in a later paper.

Summary:—

$\left[\begin{matrix}\text{Co}\end{matrix}\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right]WO_4$, $\left[\begin{matrix}\text{Co}\end{matrix}\begin{matrix}(NH_3)_5\\ Br\end{matrix}\right]WO_4$,

$\left[\begin{matrix}\text{Co}\end{matrix}\begin{matrix}(NH_3)_5\\ Cl\end{matrix}\right]MoO_4$ and $\left[\begin{matrix}\text{Co}\end{matrix}\begin{matrix}(NH_3)_5\\ Br\end{matrix}\right]MoO_4$ were prepared and analyzed.

The compound $3(NH_4)_2O{\cdot}Co_2O_3{\cdot}12MoO_3{\cdot}20H_2O$ was prepared from $\left[\begin{matrix}\text{Co}\end{matrix}\begin{matrix}(NH_3)_4\\ CO_3\end{matrix}\right]_2(SO_4){\cdot}3\ H_2O$

A green ammonium cobaltous tungstate was reported.

A method was devised for the separation of halogen from molybdenum or tungsten.

Methods for the decomposition of the complexes were tried and comparisons made of the methods for the determination of the constituents.